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Equilibrium and kinetic studies of copper (II) ion uptake by modified wheat shells

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ABSTRACT

Natural adsorbents such as shells of unmodified wheat (RW), and modified wheat (MW) were assessed for Cu(II) adsorption from aqueous solutions. The removal of Cu(II) by these adsorbents from aqueous solution was investigated by using several parameters such as modificiation, contact time, temperature and pH. The extent of Cu(II) removal increased with increasing contact time, temperature and pH and also with modification by Reactive Orange 122 of adsorbent. The experimental data were analysed by the Langmuir and Freundlich models of adsorption. It was found that the Freundlich equation fits better than the Langmuir equation. In addition, the adsorption data obtained at different temperatures of Cu(II) by adsorbents were applied to pseudo first-order, pseudo second-order and Weber-Morris equations, and the rate constants of first-order adsorption (k_1), the rate constants of second-order adsorption (k_2) and diffusion rate constants (k_3) at these temperatures were calculated, respectively. The rates of adsorption were found to conform to pseudo second-order kinetics with good correlation ($R^2 \geq 0.989$). The data obtained from adsorption isotherms at different temperatures were used to calculate some thermodynamic quantities such as free energy of adsorption ($\Delta G°$), enthalpy ($\Delta H°$), and entropy ($\Delta S°$). It is found that $\Delta G°$ is negative, indicating that the nature of adsorption process for Cu(II) is spontaneous. The positive value of $\Delta H°$ indicates that the adsorption of Cu(II) onto adsorbents is an endothermic process. The positive value of $\Delta S°$ reflects the affinity of the adsorbent for Cu(II). As a result, the present work indicates that the wheat shells MW chemically by Reactive Orange 122, possess more efficiency in adsorbing Cu(II) ions than the unmodified one (RW).

Keywords: Adsorbents; Wheat shells; Kinetics; Thermodynamics; Modification; Reactive orange 122

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1. Introduction

The presence of heavy metal ions from the transition series, viz., Cu, Fe, Ni, Pb, etc. in the environment is of major concern due to their toxicity to many life forms. Unlike organic pollutants, the majority of which are susceptible to biological degradation, metal ions do not degrade into any harmless end products [1]. Their presence in streams and lakes has been responsible for several health problems with animals, plants and human beings [2]. Since copper is a widely used material, there are many actual or potential sources of copper pollution. Copper may be found as a contaminant in food, expecially shellfish, liver, mushrooms, nuts, and chocolate. Briefly, any

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processing or container involving copper material may contaminate the products such as food, water or drink.

Copper is essential to human life and health, but like all heavy metals, is potentially toxic as well. For example, continued inhalation of copper-containing spray is linked with an increase in lung cancer among exposed workers [3].

Precipitation, ion exchange, extraction, biosorption, filtration, electrochemical treatment and adsorption are conventional methods for the removal of heavy metals from aqueous solutions. All these methods have significant disadvantages such as incomplete ion removal, high-energy requirements and production of toxic sludge or other waste products that require further disposal. Therefore, these methods do not suit the needs of developing countries [4]. Among the above mentioned methods, adsorption is considered to be relatively superior to other techniques because of low cost, simplicity of design, availibity and ability to treat dyes in more concentrated form [5]. Activated carbon is the most widely used adsorbent since it has excellent adsorption efficiency for heavy metals, but its use is usually limited due to its high cost [6]. This has led many researchers to search for cheaper substitutes such as coal, fly ash, silica gel, wool wastes, biomass, agricultural wastes, wood wastes, and clay materials. They have been applied with varying success rates in metal removal [7]. To find an effective and ideal adsorbent, researchers have exploited many low cost and biodegradable subtitutes obtainable from natural resources for the removal of different metals from aqueous solutions at different operational conditions.

At present, there is a growing interest in using low-cost, commercially available materials for the adsorption of heavy metals. A wide variety of materials such as rice husk [8] modified cellulosic materials [9], fly ash [10], modified bark [11], sawdust [12], pine bark [13], animal bones [14], holly oak [15], Pleurotus pulmonarius [16] and modified barks [17] are being used as low-cost alternatives to expensive adsorbents.

The aim of this work is to investigate the effect of several parameters such as contact time, temperature, and pH on the adsorption efficiency of Cu(II) from aqueous solutions by unmodified wheat (RW) and modified wheat (MW) shells, which are a very cheap and readily available material in most countries. The thermodynamic parameters for the adsorption of Cu(II) were computed and discussed. The kinetics and the factors controlling the adsorption process were also studied.

2. Materials and methods

2.1. Materials

The wheat shells were obtained from local wheat mills. The collected materials (the last hard layer of wheat) were then washed several times with distilled water to remove all dirt particles. The washing process was continued till the wash water contained no colour. The washed material was then dried in a hot oven at 100°C for 24 h. The dried material was then ground, using a steel mill. The adsorbent was sieved through 0.6 mm sieve. This material was subjected to cleaning by boiling it in 1 g l^{-1} soap solution for 15 min followed by thoroughly washing with water. The purified biomaterial was also loaded with Reactive Orange 122. Characteristics of the RW and MW were determined, and results are summarized in Table 1.

2.2. Chemicals

A monochlorotriazine type reactive dye, Reactive Orange 122 (Information about the chemical nature of this dye was not available from the current literature, presumably because of commercial confidentiality [18]) supplied by Aldrich was used as a commerically available powder for modification of materials. The other chemicals used, such as $CuSO_4 .5H_2O$, Na_2SO_4, Na_2CO_3, HCl, NaOH were also of Analytical Reagent grade, supplied by Merck. A stock solution of Cu(II) 1000 mg l^{-1} was prepared, which was diluted to required initial concentrations. Demineralised water was used for all experiments.

2.3. Apparatus

Absorbance values were measured with a Unicam Model 929 atomic absorption spectrometer (AAS). A pH-meter (Jenway 3010) and shaker (Nuve ST 400) were used for pH adjustment and shaking, respectively. Elemental analysis was carried out with an EA 1108 Fisons instruments. The surface area was determined by a single-point N_2 gas adsorption method by using a model micromeritics Flow Sorb. II 2300. An elemental analysis (C and H content) was carried out with an EA 1108 Fisons insruments.

2.4. Methods

2.4.1. Modification of wheat shells

One gram of the dye powder was dissolved in 100 ml of warm water in order to prepare a 1% stock solution of the dye. For dye loading of wheat shells, the procedure for dyeing of cotton textiles with reactive dyes was used [19]. Then 100 g of wheat shells was added to 4 l of the diluted solution (material to liquor ratio 1:40) containing 50 ml of the stock solution of dye at 40°C temperature, and the temperature was slowly raised to 85°C. After about 10 min, 65 g l^{-1} sodium sulphate was added in two lots in 10 min for improving the dye exhaustion onto

Table 1
Physical and chemical properties of unmodified wheat shells used in the experiments

Chemical characteristic	
Moisture content (%)	6.40
Water soluble components (%)	22.33
Insoluble components (%)	75.14
Ash (%)	2.58
Total loss of ignition (%)	88.45
C content (%)	44.59
H content (%)	6.56
pH	6.00
Physical characteristic	
Surface area (BET) (m^2 g^{-1})	0.67
Bulk density (g ml^{-1})	0.36
Particle size (mm)	0.60

Results of Bohem titration (mmol g–1)

Carboxylic	Lactonic	Phenolic	Basic	Acidic
0.146	0.020	0.842	0.00	1.008

the material. After another 20 min, for covalent fixation of the dye onto the material, 15 g l^{-1} sodium carbonate was added to the same bath and the treatment was continued at 85°C for further 30 min. At the end, the material was filtered and washed thoroughly with hot water. This was followed by treating the dye loaded material with 1 g l^{-1} soap solution at boil for 20 min and by thoroughly washing it with water to remove completely the unfixed dye and the by product of the reaction, the hydrolysed dye. The coloured material was then dried in an oven at 50°C overnight and used as adsorbent.

2.4.2. Estimation of dye loading on the materials

The estimation of the amount of dye loaded onto the wheat shells was carried out by using Shimadzu UV Spectrophotometer, model 160. Each dyestuff gives the colour absorption value at a particular λ_{max} specific to it. A calibration plot is made by using pure dye dissolved in water in which a known quantity of dye concentration (mg l^{-1}) is linearly related to its absorbance (%) value at the particular λ_{max}. The absorbance of initial dye liquor used for dye loading was measured at λ_{max} of 490 nm, (A). After completion of the dyeing process, the material was carefully removed from the bath without spilling any drop of the spent liquor. Water after washing, the soap liquor as well as final washings were carefully collected together, added to the exhausted dye bath and its absorbance was measured (B). This absorbance corresponds to the amount of dye not loaded on the adsorbent. Therefore, (A-B) is related to the dye loaded onto the material. By making use of the calibration curve, the amount of dye in mg g^{-1} of material was determined. Thus, the dye loading observed for wheat shells was 6.43 mg g^{-1}.

2.4.3. Batch adsorption experiments

Batch studies were conducted with Cu(II) solutions prepared in the laboratory. The effect of contact time on the amount of Cu(II) adsorbed was investigated at 100 mg l^{-1} initial concentration of Cu(II), at different temperatures (298, 308 and 318 K) and optimum pH (pH: 5.0). A weighed sample of RW and MW (1.0 g) was mixed with a 50 ml metal solution. For the other adsorption experiments, 50 ml of Cu(II) solution of known initial concentration (75, 100, 125, 150, 175, 200, and 225 mg l^{-1}) was shaken with a certain amount of adsorbent at desired pH and temperature at 150 rpm for 60 min. The pH of the solution was adjusted with 0.5 N HCl or 0.1 N NaOH by using a pH-meter with a combined pH electrode. The pH-meter was standardized with NBS buffers before each measurement. A constant bath was used to keep the temperature constant. At the end of the adsorption period, the solution was centrifuged for 10 min at 3000 rpm. After centrifugation, the Cu(II) concentration in the supernatant solution was analyzed, using an Atomic Absorption Spectrophotometer. The samples were pipetted from the medium reaction by the aid of a very thin point micropipette, which prevented the transition to the solution of the RW and MW samples. The amount of Cu(II) adsorbed was calculated by using the equation:

$$q_{\mathrm{e}} = \left(C_{\mathrm{i}} - C_{\mathrm{e}}\right) V/m \tag{1}$$

where q_e is the amount adsorbed per gram of adsorbent, C_i and C_e is concentration of Cu(II) (mg l^{-1}) at initial and equilibrium, respectively. V is volume solution of metal (l) and m is adsorbent dosage (g). All experiments were repeated three times, and the average values are presented in this communication (standard deviation = 0.016).

3. Results and discussion

3.1. C, H analysis

A sample of adsorbents was put in an oven at 1273 K under oxygen in order to obtain a quick and complete combustion. H_2O and CO_2 were released and conducted in a copper oven at 923 K, then passed through a 2 m column with helium vector gas, and analyzed by a catharameter detector. The results of analysis are shown in the Table 1.

3.2. Functional groups dosage

Knowing the chemical structure of the used adsorbent is important to understand the adsorption processes. The adsorption capacity of adsorbent is strongly influenced by the chemical structure of their surface [20]. The oxygenated surface groups were determined according to the method by Bohem. First, 1.0 g of adsorbent was placed in 50 ml of each of the following 0.05 N solutions: sodium hydroxide, sodium carbonate, sodium bicarbonate, and hydrochloric acid. Vials were sealed and shaken for 24 h and then 5 ml of each filtrate was pipetted; the excess of the base or acid was titrated with HCl or NaOH, as required. The numbers of acidic sites of various types were calculated on the assumption that NaOH neutralizes carboxylic, phenolic, and lactonic; Na_2CO_3 neutralizes carboxylic and lactonic groups; and $NaHCO_3$ neutralizes only carboxylic groups. The number of surface basic sites was calculated from the amount of hydrochloric acid which reacted with the adsorbent; the results of Bohem titration (numbers of acidic and basic groups) are summarized in Table 1.

During the modification process the dyestuff molecules bind to the acidic grup of adsorbent surface with non-covalent interactions. Then, we think that when the modified materials are reacted with the metal solution, the complex is formed between the dyestuff molecules and the metal ions. Therefore, the metal can be removed from solution with modified adsorbent more than with the raw adsorbent.

3.3. Other chemical-physical characteristics

Characteristics of the adsorbents such as bulk density, moisture content, ash content, solubility in water, total loss of ignition were determined. The ash content was determined by burning it in a furnace at 1173 K [20]. The results are summarized in Table 1.

3.4. Contact time

The adsorption of Cu(II) at a fixed concentration on RW and MW was studied as a function of contact time in order to determine the equilibration time for maximum adsorption. The contact time experiments were carried out at 298, 308 and 318 K temperatures. The dependence of adsorption of Cu(II) with time is presented in Fig. 1. The adsorption increased with increasing contact time, and the equilibrium was attained after shaking for 60 min. Therefore, in each experiment, the shaking time was set to 60 min.

3.5. Effect of pH

The pH of the aqueous solution is an important controlling parameter in the adsorption process [21]. In order to study the influence of pH on the adsorption capacity of RW and MW, experiments were performed by using various initial solution pH values varying from 1.0 to 6.0, with other parameters being kept constant. Fig. 2 depicts the effect of pH on adsorption of metal ions on both modified and RW shells. The removal of Cu(II) increased with increasing pH. The peak adsorption of Cu(II) was attained at pH 5.0. One of the reasons for the metal ions adsorption behaviour of the bio-adsorbent (RW and MW) is that the adsorbents surface contains a large number of active sites. The metal uptake depends on these active sites as well as on the nature of the metal ions in solution. The affinities of the

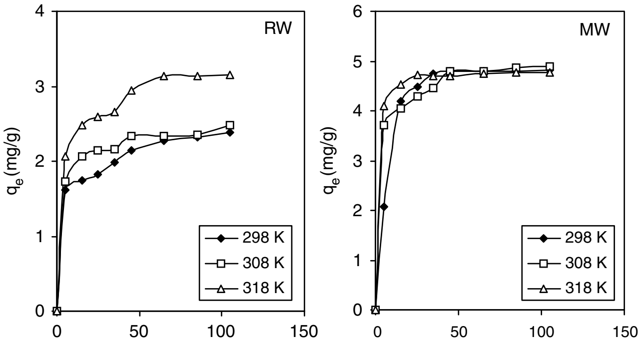

Fig. 1. Effect of contact time on the adsorption of Cu(II) at different temperatures (C_i: 100 mg l^{-1}, adsorbent: 1.0 g , agitation speed: 150 rpm, pH: 5.0).

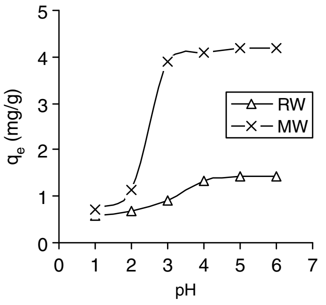

Fig. 2. The effect of pH on the adsorption of Cu(II) (C_i: 100 mg l^{-1}, t: 60 min, adsorbent: 1.0 g, agitation speed: 150 rpm).

surface sites of RW and MW depend on the nature of ions. This may be further explained in relation to a competition effect between the H_3O^+ and Cu(II) ions. At low pH values, the concentration of H_3O^+ ions is more than that of metal ions, hence the former ions occupy the binding sites on the RW and MW, leaving metal ions free in solution. When the pH increases, the concentration H_3O^+ ions decreases, and the sites on the adsorbent surface mainly turn into dissociated forms and can exchange H_3O^+ ions with metallic ions in solution [2]. As pH of the system increased, the number of negatively charged adsorbent sites increased, and the number of positively charged surface sites decreased, which did favour the adsorption of positively charged Cu(II) ions.

3.6. Effect of modification

In order to increase the adsorption capacity of wheat shells, they were modified with Reactive Orange 122. Fig. 3 shows the adsorption efficiency of modified adsorbent for Cu(II), as a function of the temperature. As seen in Fig. 3, the removal efficiency of Cu(II) from aqueous solution by wheat shells increased with modification.

3.7. Adsorption kinetics

Adsorption is a physical-chemical process that involves the mass transfer of solute (adsorbate) from the fluid phase to the adsorbent surface [22]. A study of kinetics of adsorption is desirable as it provides information about the mechanism of adsorption, which is important for efficiency of the process [23]. In order to investigate the mechanism of adsorption, characteristic constants of adsorption rate were determined, using a pseudo first-order equation of Lagergren based on solid capacity, and pseudo second-order equation based on solid phase adsorption and Weber-Morris equation. Temperature, pH, and stirring speed were constant for all experiments. The first-order rate expression of Lagergren based on solid capacity is generally expressed as follows [7]:

$$\log\left(q_\mathrm{e} - q_\mathrm{t}\right) = \log q_\mathrm{e} - \frac{k_1 t}{2.303} \tag{2}$$

where q_e is the amount adsorbed (mg g^{-1}) at equilibrium, q_t is the amount adsorbed (mg g^{-1}) at time t and k_1 is the adsorption rate constant (1 min^{-1}). The straight line of the plot of log ($q_e - q_t$) versus time confirm the applicability of the Lagergren equation for the present system [21]. The values of k_1 were determined from the slope of the plots, and are given in Table 2.

Recently, Ho and Mc Kay [24] have reported that most of the sorption systems follow a second-order kinetic model which can be expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 {q_\mathrm{eq}}^2} + \frac{t}{q_\mathrm{eq}} \tag{3}$$

where k_2 is the adsorption rate constant [g (mg min^{-1})]. The values of k_2 were determined by the intercept of the plot t/q_t versus time, and are given in Table 2.

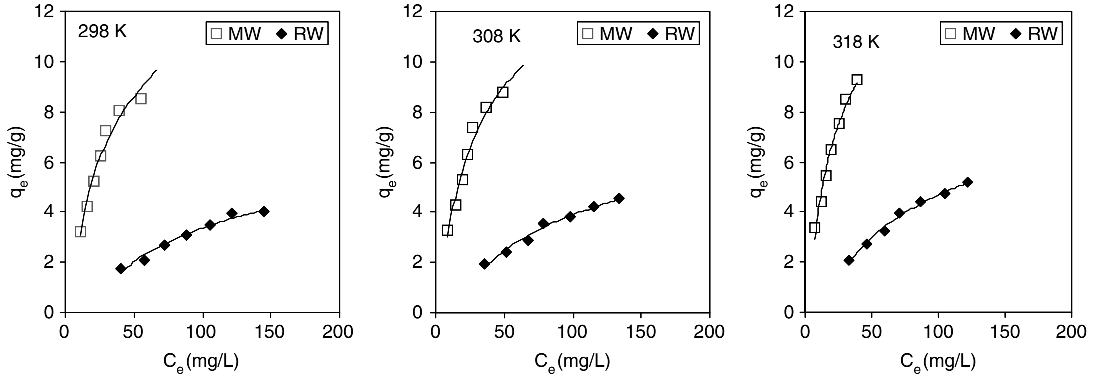

Fig. 3. Effect of modification on the adsorption of Cu(II) at different temperatures (C_i: 100 mg l^{-1}, t: 60 min, adsorbent: 1. 0 g, agitation speed: 150 rpm, pH: 5.0).

Table 2
Adsorption kinetic parameters of Cu(II) on RW and MW (Ci: 100 mg l–1, Adsorbent: 1.0 g, agitation speed: 150 rpm, pH: 5.0)

Adsorbent	First-order kinetic model				Second-order kinetic model			Diffusion		
	T (K)	k_1 (1 min^{-1})	q_{eq} (mg g^{-1})	R^2	k_2 [g (mg min)$^{-1}$]	q_{eq} (mg g^{-1})	R^2	k_3	m	R^2
RW	298	0.02	1.69	0.850	0.02	3.97	0.989	1.17	0.148	0.850
	308	0.03	1.04	0.756	0.10	4.01	0.998	1.49	0.110	0.956
	318	0.07	2.50	0.949	0.05	4.2	0.997	1.44	0.197	0.842
MW	298	0.08	2.22	0.880	0.04	5.12	0.997	1.76	0.247	0.728
	308	0.06	2.58	0.933	0.05	5.35	0.998	3.11	0.101	0.930
	318	0.06	0.97	0.797	0.25	4.81	0.999	3.91	0.048	0.825

The kinetics of adsorption can be expressed as [25]:

$$\ln q_t = \ln k_3 + m \ln t \tag{4}$$

where q_t is the amount adsorbed (mg g^{-1}) at time t (min), t is the contact time in minute, m and k_3 are constants. Slope m depicts the sorption mechanism and k_3 represents the rate factor. The values of m and k_3 were determined by the slope and the intercept of the plots lnq_t versus lnt, and are given in Table 2.

To interpret properly the experimental data, it is necessary to determine which of the steps in the sorption process governs the overall adsorption rate under the specified experimental condition.

The three consecutive steps in the adsorption of an adsorbate by a porous adsorbent are (i) transport of the adsorbate to the external surface of the adsorbent (film diffusion); (ii) transport of the adsorbate within the pores of the adsorbent (diffusion within the particle); and (iii) adsorption of the adsorbate on the exterior surface of the adsorbent. According to Weber and Moris, a value of m = 0.5 reflects intraparticle diffusion as the rate-determining step, while smaller values indicate the involvement of both of the processes, to almost equal extent [25]. In this study the value of m is less than 0.5 and the sorption rate seems to be equally dependent on both and neither of these appear to be sufficiently slow as to be the rate-determining step. As shown in Table 1, because of very low surface area (*less porous*) of the adsorbent used it is an expected result.

3.8. Adsorption model

The equilibrium adsorption isotherm is of importance in the design of adsorption systems [7]. In general, the adsorption isotherm describes how adsorbates interact with adsorbents and thus is critical in optimizing the use of adsorbents. Adsorption isotherms expressing the adsorbed amounts as a function of equilibrium concentration for different temperatures are presented in Fig. 3.

Several isotherm equations are available, and two important isotherms are selected for this study: the Langmuir and Freundlich isotherms. The Langmuir adsorption isotherm assumes that the adsorption takes place at specific homogeneous sites within the adsorbent, and it has been used successfully for many adsorption processes of monolayer adsorption. The linearized Langmuir equation is represented as follows [26]:

$$\frac{C_e}{q_e} = \frac{1}{(b.Q_m)} + \frac{C_e}{Q_m} \tag{5}$$

where b is the equilibrium constant or Langmuir constant related to the affinity of binding sites (L mg^{-1}) or (l mol^{-1}) and Q_m represents a partical limiting adsorption capacity when the surface is fully the covered with metal ions and assists in the comparison of the adsorption performance. Q_m and b are calculated from the slope and intercept of the straight lines of plot C_e/q_e versus C_e.

The Freundlich isotherm is an empirical equation employed to describe heterogeneous systems. The Freundlich isotherm is given in logaritmic form as [26]:

$$\log q_e = \log K_F + (1/n).\log C_e \tag{6}$$

where K_F is roughly an indicator of the adsorption and $(1/n)$ of the adsorption intensity. K_F and n can be determined from the linear plot of log q_e versus log C_e.

Adsorption isotherms were obtained in terms of Eqs. (5) and (6) by using experimental adsorption results in these equations. The values Q_m, b, K_F, and n are summarized in Table 3. The isotherm data were calculated from the least square method and the related correlation coefficients (R^2 values) are given in the same table. As seen from Table 3, the Freundlich equation represents the adsorption process very well; the R^2 values were all higher than 0.973, indicating a very good mathematical fit. As seen in Table 3, the maximum adsorption capacities, Q_m, for Cu(II) onto RW and MW at 298, 308 and

Table 3
Langmuir and Freundlich isotherm constants for adsorption of Cu(II) on RW and MW (t: 60 min, adsorbent: 1.0 g, agitation speed: 150 rpm, pH: 5.0)

	Langmuir constants				Freundlich constants			
	T (K)	b (l mg^{-1})	Q_m (mg g^{-1})	R_L (C_i: 100 mg l^{-1})	R^2	K_F	n	R^2
RH	298	0.002	8.51	0.833	0.915	0.129	1.424	0.982
	308	0.004	12.44	0.714	0.811	0.175	1.491	0.984
	318	0.006	13.61	0.625	0.877	0.595	1.408	0.981
MH	298	0.026	15.22	0.278	0.938	0.740	1.561	0.973
	308	0.029	15.30	0.256	0.951	0.852	1.611	0.978
	318	0.030	17.42	0.250	0.972	0.926	1.559	0.992

318 K were found to be 8.51, 12.44, and 13.61; 15.22, 15.30, and 17.42 mg g^{-1}, respectively. Maximum adsorption capacities of the adsorbents rise with increase in the temperature.

K_F is an Freundlich constant that shows adsorption efficiency of adsorbent, n is a constant which shows the extent of relationship between adsorbate and adsorbent [7]. The value K_F of RW and MW for Cu(II) at 298, 308 and 318 K are 0.129, 0.175, and 0.595; 0.740, 0.852, and 0.926, respectively. It is generally reported that the values of n in the range 1–10 represent good adsorption [21]. In the present work, the exponent was $1< n < 10$, indicating favourable adsorption.

The essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor "R_L" which is defined by the following relationships [8] given by:

$$R_L = \frac{1}{\left(1 + b.C_i\right)} \tag{7}$$

According to the value of R_L the isotherm shape may be interpreted as follows:

Value of R_L	Type of adsorption
$R_L > 1.0$	Unfavourable
$R_L = 1.0$	Linear
$1 > R_L > 0$	Favourable
$R_L = 0$	Irreversible

The results given in Table 3 show that the adsorption of Cu(II) on RW and MW is fovourable. As also seen in Table 3, the maximum adsorption of RW and MW for Cu(II) varied between 8.51 and 13.61; 15.22 and 17.42 mg g^{-1}, respectively.

Previously, some researchers have investigated several adsorbents such as diatomite and modified diatomite [17], fly ash [10], sawdust [3], Pleurotus pulmonarius[16], peat [27], tea-industry waste [28], Rubber leaf powder [30], Rubber wood sawdust [31], Hazelnut husk A.C. [32], Carboxymethylated Chitosan Hydrogel Beads [33], chitosan hydrogel beads [34] and the shells of hazelnut modified with Reactive Orange [40] for the removal of Cu(II). By comparison of the results obtained in this study with those in the prviously reported works (Table 4) on adsorption capacities of various low-cost adsorbent in aqueous solution for Cu(II), it can be stated that our findings are good.

3.9. SEM

Fig. 4 shows the SEM (Scaning electron microscopy) micrographs of RW. As it is known, SEM is one of the most widely used surface diagnostic tools. RW has heterogeneous surface.

Table 4
Previously reported adsorption capacities of various low-cost adsorbents for Cu(II)

Low-cost adsorbents	Adsorption capacity (mg g^{-1})	Ref.
Diatomite	27.55	17
Modified diatomite	55.56	17
Fly ash	1.54	10
Sawdust	1.79	3
Peat	12.07	27
Tea-industry waste	8.64	28
Rubber leaf powder	8.92	30
Pleurotus pulmonarius	6.203	16
Rubber wood sawdust	5.729	31
Hazelnut husk A.C.	6.645	32
Unmodified wheat shells (RW)	13.61	In this study
Modified wheat shells (MW)	17.42	In this study

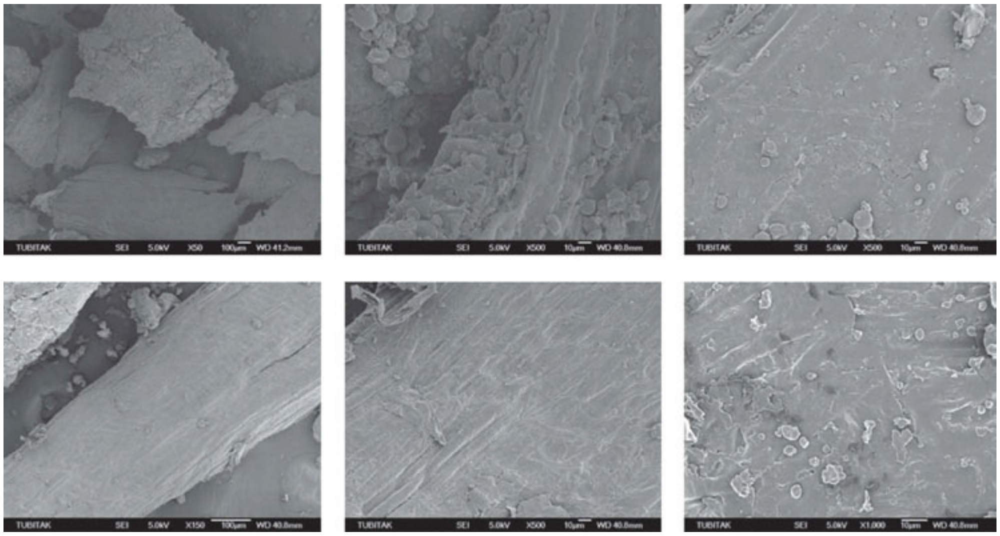

Fig. 4. The SEM micrographs of RW.

3.10. Estimation of thermodynamic parameters

To determine the effect of temperature on the adsorption of Cu(II), the experiments were also conducted at 298, 308, and 318 K at temperature are shown in Fig. 3. The degree of adsorption increases with increased temperature, indicating that the adsorption is endothermic [29]. The free energy of adsorption (ΔG°) can be related to the equilibrium constant K (l mol^{-1}), corresponding to the reciprocal of the Langmuir constant, b, by the following equation. The values of free energy change (Δ*G*°), enthalpy change (Δ*H*°), and entropy change (Δ*S*°), for the adsorption process were calculated, using the equations [7,29]:

$$\Delta G^{\circ} = -\,RT \ln b \tag{8}$$

$$\ln b = \frac{\Delta S^{\circ}}{R} - \frac{\Delta H^{\circ}}{RT} \tag{9}$$

Thus, a plot of ln b vs $1/T$ should be a straight line. Δ*H*° and Δ*S*° values were obtained from the slope and intercept of this the plot, respectively [7]. Δ*G*°, Δ*H*° and Δ*S*° were obtained from the Eqs. (8,9) and are given in Table 5.

Negative values of Δ*G*° indicate the feasibility of the process and spontaneous nature of the adsorption with a high performance of Cu(II) for both RW and MW. Positive value of Δ*H*° indicates the endothermic nature of the process, while positive value of ΔS° reflects the affinity of the adsorbents for the Cu(II) ions, suggesting some structural changes in adsorbate and adsorbent [10]. The reason behind the positive value to the entropy can be due to dissolution of surface hydration water, initially present on wheat surface, due to Cu ions adsorption, represents a higher increase in entropy than the accumulation of Cu ions on this very surface. In other words, much more than 1 molecule of water would be displaced to the bulk phase for each Cu ion adsorbed.

Table 5
Values of thermodynamic parameters for the adsorption of Cu(II) on RW and MW (t: 60 min, Adsorbent: 1.0 g, agitation speed: 150 rpm, pH: 5.0)

Adsorbent	*T* (K)	b (l mg^{-1})	b (l mol^{-1})	Δ*G* (kj mol^{-1})	Δ*H* (kj mol^{-1})	Δ*S* (j mol K^{-1})
RW	298	0.002	127.00	–12.001	10.01	76.24
	308	0.004	254.00	–14.179		
	318	0.006	381.00	–15.711		
MW	298	0.026	1651.00	–18.357	4.35	76.55
	308	0.029	1841.50	–19.252		
	318	0.030	2476.50	–20.660		

4. Conclusions

The removal of Cu(II) *from aqueous solution* is highly dependent on contact time, temperature and pH. The amount of Cu(II) uptake (mg g^{-1}) on adsorbents was found to increase with increase in contact time, temperature, and pH. It was found that the Freundlich equation fits better than the Langmuir equation. In addition, the kinetic data were best described by the pseudo-second order kinetic model. The data obtained from adsorption isotherms at different temperatures were used to calculate thermodynamic quantities such as $\Delta G°$, $\Delta H°$, and $\Delta S°$. The results indicate that the adsorption of Cu(II) onto RW and MW is spontaneous and physical in nature.

As a result, the present work indicates that the wheat sheels modified (MW) chemically by Reactive Orange 122, possess more efficiency in adsorbing Cu(II) ions than the unmodified one (RW). The wheat shells (modified and unmodified), being a cheap and easily available material, could be an alternative for more costly adsorbents used for removal of Cu(II) from aqueous systems for environmental cleaning.

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